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Microstructural analyses of amorphic diamond, *i*-C, and amorphous carbon

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Recent experiments have identified the microstructure of amorphic diamond with a model of packed nodules of amorphous diamond expected theoretically. However, this success has left in doubt the relationship of amorphic diamond to other noncrystalline forms of carbon. This work reports the comparative examinations of the microstructures of samples of amorphic diamond, *i*-C, and amorphous carbon. Four distinct morphologies were found that correlated closely with the energy densities used in preparing the different materials.

I. INTRODUCTION

The last few years have seen a rapid growth in the number of efforts directed at the development and exploitation of thin diamond films. However, most of the work continues to be done with techniques of chemical vapor deposition (CVD) and its variants that use hydrogen in the growth process.¹ Invariably the results are mixtures of two products, a polycrystalline form of diamond and noncrystalline materials which seem to be hard, carbon-rich plastics. These amorphous forms retain substantial amounts of hydrogen that vary from 20% to 60% in the finished films. Common usage has fixed the inappropriate name of diamondlike carbon (DLC) onto these materials, despite the preponderance of hydrogen in them. Probably because of the pervasiveness of the CVD methodologies, the general impression has developed that polycrystalline diamond and DLC are the only possible products of technologies that try to produce thin-film diamond. However, other noncrystalline carbons have been prepared without hydrogen and found to have diamondlike properties as well.

Angus and Hayman¹ have used the term *a*-C to describe all of the diverse types of amorphous materials made only from carbon with some sp^3 bonding and Merz, Hoffmann, and Balaban² have indicated how very many distinct structures such a designation might span. Weissmantel³ has tended to prefer the term *i*-C for the subset of *a*-C produced from ionized precursors.

As early as 1971, Aisenberg and Chabot⁴ had reported that the quenching of a beam of C^+ ions in the presence of Ar and Ar^+ onto a cold substrate formed an amorphous layer having some of the properties of diamond. Subsequent work⁵⁻⁸ seemed to indicate that the *i*-C materials were closer to diamond in their properties such as hardness than were the *a*-C products of processes not involving the ionization of carbon. However, the internal structures responsible for these differences were not elucidated.

Only three structures of carbon atoms can be formed entirely with sp^3 bonding. Two are crystalline, cubic and hexagonal, and the third is amorphous diamond composed of a continuous random network of sp^3 -bonded carbon atoms. Because of the internal stresses produced by distortions of the bond angles in a truly random net, it has seemed unlikely¹ that amorphous diamond could exist as a "bulk material." However, an amorphous material is still amorphous even if it is mechanically stable only in thin films or powders. Nodules, flakes, fibers, or other nanophase elements could be composed of amorphous diamond and then be incorporated into macroscopic constructions. Stress in such composites would be much less and the number of possible combinations of these basic building blocks could conceivably accommodate the breadth of properties already found in the noncrystalline carbons having some of the properties of diamond.

Recently, we reported the first construction from amorphous diamond. That material consisted of densely packed nodules of amorphous diamond that were bonded together by mixed carbon polytypes.⁹⁻¹¹ More recently, very thin homogeneous lamina have also been reported,^{12,13} but internal stresses prevented them from being grown to appreciable thicknesses. It is interesting that the maximum thickness reported for the pure lamina is very comparable to the characteristic sizes of the nodules in the composite.

Termed amorphic diamond,^{14,15} the first material was produced by accelerating and quenching an intense laser plasma of carbon ions onto a cold substrate.¹⁶⁻¹⁸ It has been prepared with varying proportions of sp^2 -bonded carbon between the grains and different efficiencies of packing them. The grain size varies from about 200 to 1000 Å and the diamond character has been attested by the agreement of structural morphology, density, optical properties, $K\alpha$ line energies, hydrogen content, and hardness.⁹ A range of properties has been found that seems to correlate with the packing density of the diamond nodules. The better the packing, the closer the mechanical properties approach

those of crystalline diamond. Moreover, the diagnostics have agreed in assigning a composition of about 75% diamond to the samples most easily produced with the laser plasma deposition system.⁹⁻¹¹

The importance of this amorphous diamond material was emphasized by reports^{14,15} that it offered some unique advantages over even the crystalline CVD films of diamond when used in infrared (IR) applications. There were no CH absorption bands with which to contend, scattering losses were minimal, and films adhered better to advanced IR materials such as Ge and ZnS. Internal stress in a finished film is typically¹⁹ 0.86 GPa, an order of magnitude less than what has been reported for pure lamina of amorphous diamond.¹² This allows amorphous diamond films as thick as 5.0 μm to be securely bonded through an interfacial layer of alloyed or compounded chemical composition¹⁹⁻²¹ to difficult substrates such as ZnS or Ti. Such a coating provides an increase in the lifetime^{19,20} against erosive particle fluxes by factors of 100–1000. Windows of ZnS coated with 4 μm thickness of amorphous diamond have withstood²¹ 20 min exposure to rain droplets of 1.8 mm in diameter incident at speeds of 750 km h^{-1} .

While the structure and properties of amorphous diamond are in close agreement with the model of a composite, the relationships to other amorphous forms of carbon have been less clear. It is the purpose of this work to show which of the theoretically expected forms were left to describe *a*-C and *i*-C. In particular we examined the microstructures of amorphous diamond, *i*-C, and amorphous carbon deposited upon equivalent substrates. The first was prepared from C^{3+} and C^{4+} incident at keV energies,^{9,22,23} the second from C^+ incident at comparable energies, and the third from neutral C produced by thermal evaporation. Each was found to have uniquely different structural morphologies. While amorphous diamond and some of the *i*-C seemed to have one common feature in the development of nodules of sp^3 -bonded carbon, the amorphous carbon was totally different.

II. SAMPLE PREPARATION AND EXPERIMENTAL METHODS

In the work reported here a laser plasma system at the University of Texas at Dallas (UTD) was used for the deposition of amorphous diamond. As described previously,^{9,14,15,17} a Q-switched Nd-YAG laser was used to deliver 250–1400 mJ to a graphite feedstock in a UHV system at a repetition rate of 10 Hz. The beam was focused to a diameter chosen to keep the intensity on the target near $5 \times 10^{11} \text{ W cm}^{-2}$ and the graphite was moved so that each ablation occurred from a new surface. A high-current discharge confined to the path of the laser-ignited plasma was used to heat and process the ion flux further. Discharge current densities typically reached 10^5 – 10^6 A cm^{-2} through the area of the laser focus, but the laser power alone was sufficient to insure that the resulting plasma was fully ionized.^{22,24}

Substrates exposed to the ion fluxes emerging from the hotter core of the plasma were coated with amorphous dia-

mond while surfaces illuminated only by the cooler margins of the plasma grew layers of graphite, perhaps defected graphite as suggested by Tamor and Wu.²⁵ A planetary drive system for rotating substrates within the cone exposed only to ions from the plasma core insured the simultaneous deposition of uniform layers of amorphous diamond over several substrate disks 30 mm in diameter. Growth rates of $0.5 \mu\text{m h}^{-1}$ over 100 cm^2 areas have been realized on untreated substrates of a variety of materials including Si, Ge, ZnS, Cu, stainless steel, quartz, glass, and plastics. Despite the relatively high ion fluxes, bulk temperatures of the substrates did not exceed 35 °C over deposition periods of hours. Films have been grown to thicknesses of 5 μm and to date over 1000 samples have been prepared under a variety of plasma conditions.

The tool for comparative studies of structure was a Nanoscope II, scanning tunneling microscope (STM) located at UTD. Because of the relatively low conductivity of the films the use of STM was particularly difficult. In previous work thin films deposited on high-conductivity Si had been successfully imaged¹⁴ but better results were subsequently obtained with layers grown on front-surface mirrors.⁹ The Al coating provided a usable ground plane in areas where the C^{+m} ion flux had cleaned the surface of Al_2O_3 during deposition of the film. The coating condensed from the ions protected the surface from reoxidation and imaging could be done in air. Considerable care had to be taken to avoid the tendency of aberrant growths of towers or whiskers of conductive graphite on the diamond surface to scan the STM tip rather than the reverse.

The *i*-C films were also grown on Al mirrors with the ion implantation system PARIS built at CSNSM. This device can produce positive ion beams of any element in a residual vacuum of 10^{-7} Torr. The beams are filtered in mass and energy, focused to about 1 mm in diameter, and scanned over areas up to 10 cm^2 . Resolution is 1 unit of mass and 20 eV of energy.

The C^+ beams used to produce the *i*-C samples used in this work were accelerated to relatively low energies. The use of ion current densities in the range of 10 – $100 \mu\text{A cm}^{-2}$ avoided any heating of conductive substrates such as Al. Specimens were irradiated with a normal fluence of 10^{18} ions cm^{-2} at energies of either 500 or 2000 eV. Part of the deposited carbon was sputtered away leaving an areal density for such conditions of implantation of 0.9 and $0.5 \times 10^{18} \text{ cm}^{-2}$, respectively. A bulk density of $(0.95 \pm 0.05) \times 10^{23} \text{ atoms cm}^{-3}$ was deduced from a combination of ellipsometry, interferometry, and Rutherford backscattering spectrometry (RBS) measurements. This was typical of amorphous carbon films containing substantial void fractions. The purity of the samples was attested by RBS and nuclear reaction analysis (NRA) of $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ which showed a hydrogen content always less than 0.5% and no other contaminant.

Recently it has been reported²⁶ that *i*-C films can be classified into one of two categories depending upon the energy of implantation of the C^+ . Measurements of the dielectric constant by means of spectroscopic ellipsometry and of the energy of the $K\alpha$ emission line of C with soft-

x-ray spectroscopy provide a clear distinction between members of the two categories. Regardless of thickness, *i*-C films deposited at implantation energies of 1 keV and above exhibit optical band gaps and $K\alpha$ line shifts that agree in indicating estimated contents of sp^3 bonding around 70%. In contrast, the films grown at lower energies of implantation are essentially graphitic,²⁷ everywhere above an initial interfacial layer which may be SiC on Si substrates. Measurements of electrical resistivities support this distinction showing these graphitic films to be of completely metallic character. The behavior of the *i*-C films deposited at higher energies follows Mott's $T^{1/4}$ law up to room temperature²⁸ because they contain short paths for conduction with a mean hopping distance of about 20 Å. Both types of *i*-C films were studied in the work reported here.

Since the amorphous carbon films were prepared without ionization, it was a concern that the incident flux of carbon would not succeed in stripping the Al_2O_3 from the standard substrates used for the collection of amorphous diamond and *i*-C films. For this reason the amorphous carbon films were prepared by a different method that had been customarily used to deposit free-standing stages upon which to place objects for examination by scanning electron microscopy (SEM) or by transmission electron microscopy (TEM). These carbon films were prepared at LAP/TUD. They were grown by evaporating carbon onto glass plates using an arc discharge. After deposition the films were floated off the glass plates and mounted on Cu grids.

With all three types of samples, amorphous diamond, *i*-C, and amorphous carbon films, the return of current through the ground plane or supporting grid was sufficient to permit imaging with STM at relatively low bias voltages. In earlier reports^{9-11,14} of the imaging of amorphous diamond films with STM it was mentioned that relatively high voltages had to be applied to the STM probe. The resulting elastic fields developed over such small dimensions were often sufficient to erode away material exposed at the surface. This possibility of altering the surface while examining it was recently brought under control.⁹ The use of tunneling currents inferior to 0.5 nA at voltages not exceeding 700 mV insured a lifetime of hours for features examined on a scale of $1 \mu m^2$ or larger. Higher voltages and currents could be intentionally used to erode away softer components on a much shorter scale of times reaching down to minutes. In the work reported here the surface structures were independent of the currents and voltages used to obtain the images. The only effects of successively higher values were to give shortened lifetimes to the original surfaces. Unless a specific modification is identified, the following images present original surfaces which were scanned many successive times without any detectable changes over a period of the order of 1 h.

As described in the following section, the result of examining the samples of amorphous diamond, *i*-C, and amorphous carbon was to identify four distinctive morphologies. The data presented there were not taken in the order displayed and there is a vanishingly small chance that those four structures reflect four successive conditions of

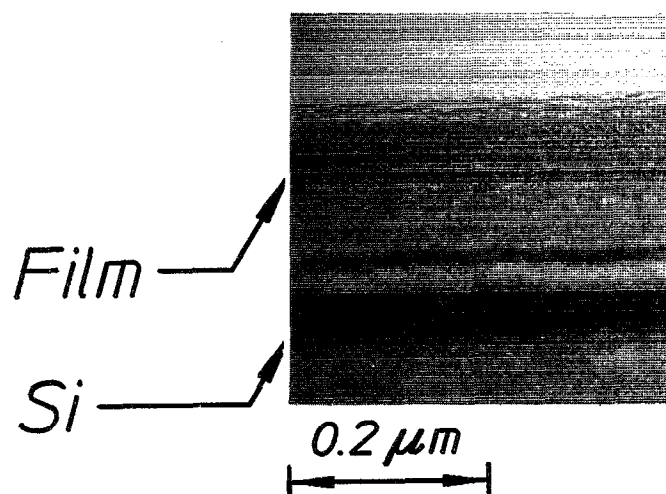


FIG. 1. Typical transmission electron microscopy (TEM) image of a thinned sample of 150 Å of amorphous diamond on Si(110) sliced to show the cross section.

the tip used in the STM examinations. On a particular sample the data were reproducible to within the resolution shown. While the same places could not be found after moving a particular specimen out of and back into the STM apparatus, the classes of structures were reproducible. A sample of defective graphite removed to permit the examination of a film of amorphous diamond would show the same type of structure when it was returned to the STM, whether or not the scanning tip had been changed. Throughout the course of the work reported here, numerous exchanges of the samples were made to avoid the possible misidentification of a characteristic pattern with a particular sample instead of with an accidentally altered or patterned tip.

III. SAMPLE STRUCTURES

The low atomic number of carbon together with the small scale of texture found in amorphous samples has tended to discourage structural studies of amorphous diamond, *i*-C, and *a*-C by the means normally used to study CVD diamond. Figure 1 shows a cross section made with TEM on a sample of amorphous diamond 150 Å thick on Si(110), but the sample could just as well have been *i*-C or *a*-C. The appearance would have been the same. This absence of any structure seen in transmission has supported the frequent suppositions that all three materials are the same. However, STM has readily shown that even amorphous diamond can be prepared with a variety of arrangements and packings of the nodules of the sp^3 -bonded carbon.⁹

One of the strongest distinctions between the types of amorphous diamond reported earlier⁹ was found to depend upon the energies of the ions condensed from the laser plasma. Relatively clear films of high mass density were condensed from ions passing through the hotter core of the laser ablation plume. In contrast very dark layers were deposited by materials grazing only through the cooler pe-

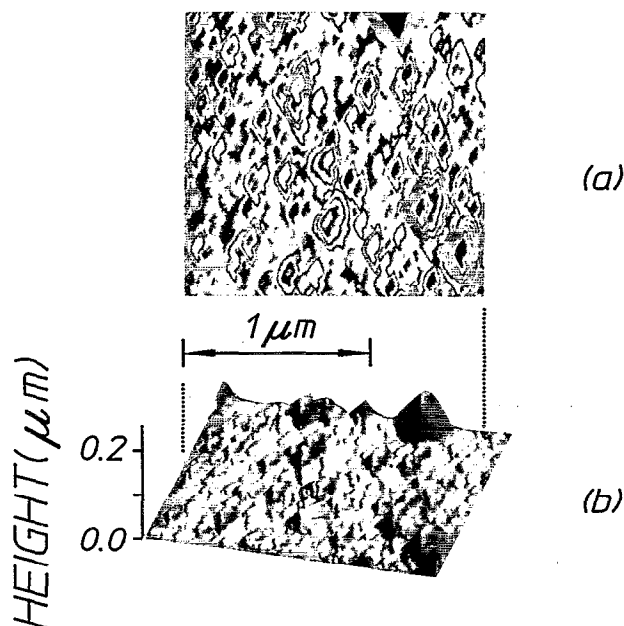


FIG. 2. Images prepared from a raster scan of heights measured with STM on a film of carbon condensed from material passing the periphery of an ablation plume at an angle of 60° from the normal to the feedstock. (a) Top view of the surface with the scale of distances shown. A periodic mapping from height to the shade of black and white has been used to produce a contour map of features. The vertical distance between contours is 8.2 nm. (b) Synthesis of an isometric view of the surface with the scale of heights above an arbitrary zero as shown, and with hypothetical lighting from the right-hand side.

riphery of the plume at an angle of 60° from the normal to the feedstock. The microstructure of the film grown at the periphery of the laser plasma looked very graphitic and showed none of the hardened nodules associated with sp^3 bonding. Now, we have found that the i -C material deposited by C^+ ions at relatively low energies of 500 eV has the same apparent structure.

Figures 2 and 3 compare the isometric reconstructions and topviews of samples of the mechanically soft materials condensed from precursors emitted from the cooler parts of a laser plasma and deposited by lower-energy C^+ ion beams, respectively, on the same types of substrates. These images are remarkably similar for such dissimilar origins and look very graphitic. The principal difference in appearances of the isometric views results from the change from "sidelighting" to "backlighting" of the reconstructed image to increase the sense of perspective. Other studies have reported graphitic properties^{26,27} for such films and the small scale and uniformity of the platelike structures seen here suggest an identification of this material with the type of defective graphite predicted by Tamor and Wu.²⁵ In any case, this form condensed from low-energy C^+ ions is not amorphous diamond as described by earlier theory and experiment.^{9-11,14,15,26,29}

Completely distinct from the "defective graphite" seen in Figs. 2 and 3 was the true amorphous carbon. Even this traditionally "structureless" film for support of electron microscopy subjects was not without texture. Shown in

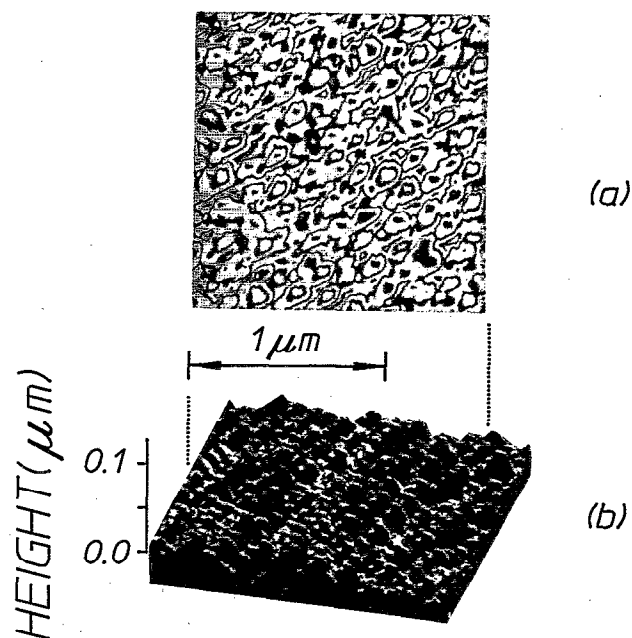


FIG. 3. Images prepared from a raster scan of heights measured with STM on a film condensed to a nominal dose of 10^{18} cm^{-2} from an ion-beam flux of C^+ carrying 500 eV kinetic energy. (a) Top view of the surface produced with a periodic mapping from height to the shade of black and white. The vertical distance between contours is 15.8 nm. (b) Synthesis of an isometric view of the surface with the scale of heights above an arbitrary zero as shown, and with hypothetical lighting from the back.

Fig. 4 is the surface found for amorphous carbon under the same conditions of examination. Partitioned by a web of deep cracks, the superficial appearance was analogous to that of a sheet of drying mud. The origin of the cracks can be readily interpreted as being mechanical since the film was unsupported over distances great in comparison to its thickness. There was no evidence of either the defective or broken graphitic plates of Figs. 2 and 3 nor of the nodules of sp^3 bonding. The amorphous carbon film was comparatively fragile and readily eroded by the imaging process. Figure 5 shows the damage produced by only four successive raster scans of the darkened area in 3 min at a bias voltage of 2000 mV and a tunneling current of 1.0 nA. Most probably this form of a -C is simply packed soot.

Completely different morphologies were found for the samples of amorphous diamond and i -C deposited from high-energy ions onto the same types of substrates. Not only were they distinct from each other, but they were drastically different from the structures found for defective graphite and for amorphous carbon. Figures 6 and 7 compare the results of examination of samples of amorphous diamond prepared from the high-energy C^{3+} and C^{4+} ions from the core of the laser plasma and of samples of i -C condensed from C^+ ions carrying 2000 eV, respectively. Reconstructed isometric images and topviews are shown to the same scales for each. The amorphous diamond was about 2000 Å thick and the i -C sample about 700 Å.

As reported previously,⁹ the amorphous diamond has a single structure of closely packed nodules having roughly

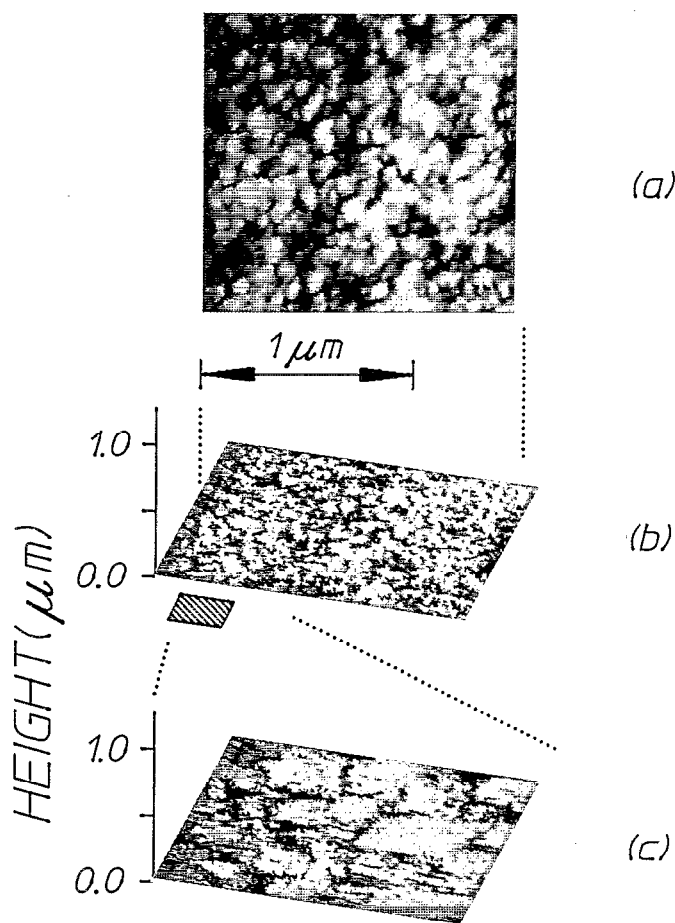


FIG. 4. Images prepared from a raster scan of heights measured with STM on a film of amorphous carbon. (a) Top view of the surface with the scale of distances within the plane as shown. A monotonic mapping from height to the shade of black and white has been used to span a range of 12 nm. More extreme heights or depths saturate as white or black, respectively. (b) Synthesis of an isometric view of the surface with the scale of heights above an arbitrary zero as shown using the same scale of distances in the plane as in (a). (c) Magnified isometric view of the region shown schematically below (b) as shaded.

comparable sizes near 1000 Å. In contrast, the *i*-C film can be seen to consist of a reasonably level plane into which has been processed meandering channels, long in comparison to either width or depth. The channels seem to contain comparatively irregular nodules. Previous work has demonstrated substantial resistance to mechanical wear of both amorphous diamond¹⁹ and *i*-C films²⁶ and in the former case this has been identified with the nodules. The nodules in amorphous diamond are composed⁹ of predominantly sp^3 -bonded carbon and so it is not surprising to find this same type of structural unit in both materials having so many of the properties of diamond.

IV. CONCLUSIONS

While definitive conclusions are difficult to draw from structural examinations alone, nevertheless appearances can convey a great amount of useful information. The images obtained in this work present morphologies that help

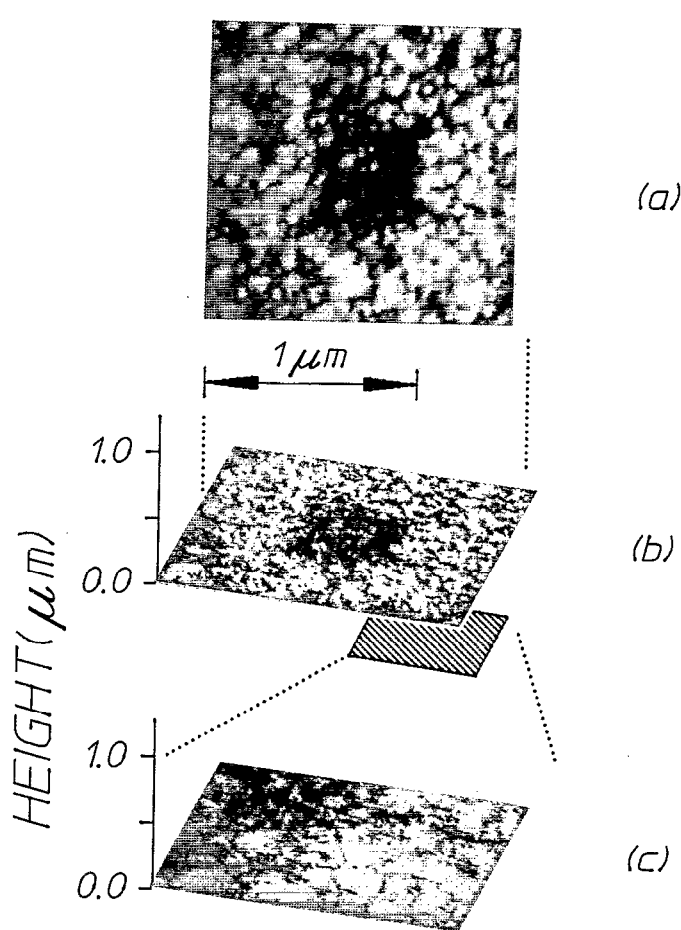


FIG. 5. Images prepared from a raster scan of heights measured with STM on a film of amorphous carbon after it was damaged by high electric fields deliberately introduced into the scanning sequence. (a) Topview of the surface with the scale of distances within the plane as shown. A monotonic mapping from height to the shade of black and white has been used to span a range of 12 nm. More extreme heights or depths saturate as white or black, respectively. (b) Synthesis of an isometric view of the surface with the scale of heights above an arbitrary zero as shown using the same scale of distances in the plane as in (a). (c) Magnified isometric view of the region shown schematically below (b) as shaded.

to refine hypotheses relating amorphous diamond, *i*-C, and amorphous carbon to the forms of carbon expected theoretically.

The films of amorphous carbon, α -C, prepared without ionization seem to be packed soot of little further interest in the development of thin-film diamond. The appearances of the *i*-C materials condensed both from low-energy ion beams and from the cooler parts of laser plasmas are remarkable in their similarity to broken or defective graphite. We tentatively identify this form with the defected graphite predicted by Tamor and Wu.²⁵

Of greatest interest are the two materials condensed from high-energy ions that show nodules. In amorphous diamond the nodules have already been identified with regions of sp^3 -bonded carbon.⁹ The strong resemblance of the nodules in the channels distributed over the surface of the *i*-C film produced at 2 keV motivates our hypothesis that they too are composed of predominantly sp^3 -bonded carbon. The plateau regions between the channels might be

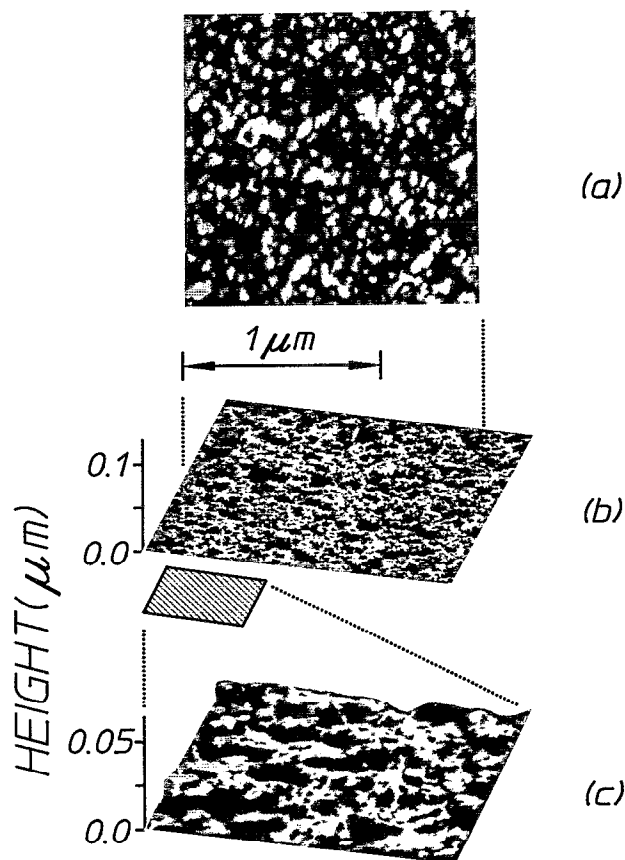


FIG. 6. Images prepared from a raster scan of heights measured with STM on a film of amorphous diamond $0.2 \mu\text{m}$ thick with a high density of 2.89 g cm^{-3} . (a) Topview of the surface with the scale of distances within the plane as shown. A periodic mapping from height to the shade of black and white has been used to produce a contour map of features. Vertical distance between contours is 15.8 nm . (b) Synthesis of an isometric view of the surface with the scale of heights above an arbitrary zero as shown using the same scale of distances within the plane as in (a). (c) Enlarged isometric view of the region shown schematically below (b) as shaded.

understood as carbon not yet processed to nodules.

In the early experiments⁴ of condensing C^+ ions to make films with some of the properties of diamond, auxiliary bombardment of the condensate with Ar^{+} was used to break up regions in which weaker bonding by sp^2 was prevalent. In this way the function of building a layer by increased condensation was separated from the combined processes of breaking sp^2 bonds and encouraging localized regions of sp^3 bonding by implanted overconstraint.⁹ However, if the same carbon ion flux must do both jobs, the competition between the layering of additional thicknesses and the converting of older layers to sp^3 nodules is less controlled. Then, it could be the case that fluxes of C^+ ions and C^{4+} ions carrying comparable kinetic energies could reach quite different balances between the growth of new materials and the processing of old. What may be seen in Figs. 6 and 7 might be the more nearly complete conversion to sp^3 -bonded nodules made possible by the greater potential energies of the C^{4+} and C^{3+} relative to the C^+ . Future work will be needed to resolve this possibility.

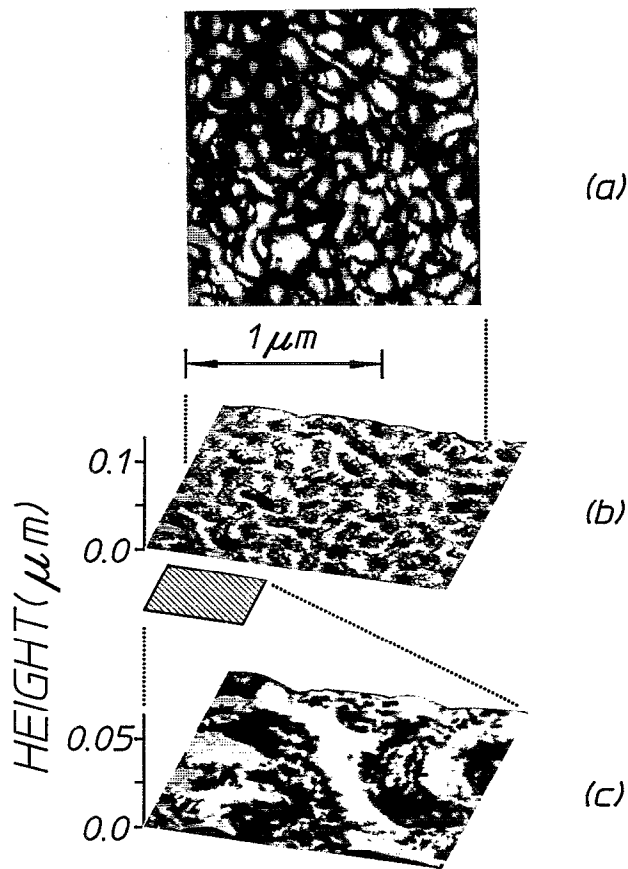


FIG. 7. Images prepared from a raster scan of heights measured with STM on a film of $i\text{-C}$ corresponding to a nominal dose of 10^{18} cm^{-2} quenched from an ion beam of C^+ at 2 keV . (a) Top view of the surface with the scale of distances within the plane as shown. A periodic mapping from height to the shade of black and white has been used to produce a contour map of features. The vertical distance between contours is 15.8 nm . (b) Synthesis of an isometric view of the surface with the scale of heights above an arbitrary zero as shown and the same scale of distances within the plane as in (a). (c) Enlarged isometric view of the region shown schematically below (b) as shaded.

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